

PATENT SPECIFICATION

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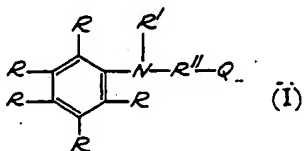


(54) IMPROVEMENTS IN OR RELATING TO HERBICIDAL AROMATIC AMINES

(71) We, HERCULES INCORPORATED, a corporation organized under the laws of the State of Delaware, one of the United States of America, of 910 Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to aromatic amines, some being novel compounds, for controlling weeds, and herbicides comprising such amines as the active ingredients alone or in combination with other herbicides.

The compounds contemplated broadly in this invention as useful in weed control are N-substituted N-phenylamines having the formula

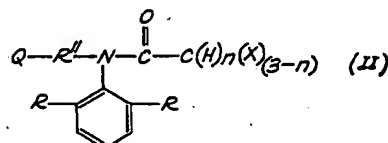


in which each R is hydrogen, halo, nitro, trihalomethyl, C₁—C₇ alkyl or C₁—C₇ alkoxy, R' is hydrogen or mono- di- or trihaloacetyl, R'' is C₁—C₇ alkylene or C₂—C₇ alkylidene, and Q is carboxyl, or salts or C₁—C₇ alkanol esters thereof, amide, mono- or di-substituted amide in which the substituents are C₁—C₇ alkyl or aryl, carbonylhydrazide or 1-substituted carbonylhydrazide in which the substituents are C₁—C₇ alkyl or aryl, with the proviso that

R' is not hydrogen when Q is amide, substituted amide, carbonylhydrazide or substituted carbonylhydrazide.

In the foregoing formula, preferred compounds are represented when the Rs at the "2" and "6" positions are C₂H₅, the remaining Rs are H, R' is H or Cl—CH₂—C(=O), R'' is CH₂ and Q is CO—O—C₂H₅.

As novel compounds within the foregoing class the invention provides compounds of the formula



in which each R, which can be the same as or different from the other, is C₁—C₇ alkyl, R'' is C₁—C₇ alkylene or C₂—C₇ alkylidene, and Q is C₁—C₇ alkoxy, carbonyl, amide, mono- or di-substituted amide in which the substituents are selected from C₁—C₇ alkyl and aryl, carbonylhydrazide or 1-substituted carbonylhydrazides in which the substituents are selected from C₁—C₇ alkyl and aryl, X is halo, and n is 0, 1 or 2.

In a further aspect of this invention there is provided a herbicidal composition comprising a mixture of an N-phenylamine as defined broadly above and "application aid" material.

"Application aid" material is generally inert material that facilitates distribution or dispersion of the phytotoxic mixture when it is applied to soil or to foliage of undesirable

plants. It encompasses diluents, carriers, extenders, surfactants, spreading agents, sticking agents and wind drift control agents.

Also, according to the invention, a process for controlling grassy weeds comprises applying an effective quantity of one of the said N-phenylamines or the said herbicidal composition to the habitat of said weeds.

The N-phenylamines according to the invention have both pre- and post-emergence toxicity to grassy weeds, and at concentrations at which they kill or prevent growth of grassy weeds a number of desirable crop plants are relatively unaffected by them. However, broadleaf weeds in general appear to have a greater tolerance to these compounds at these concentrations than grassy weeds. Consequently, when the N-phenylamines according to the invention are applied to the habitat of both kinds of weeds it is desirable to apply at about the same time other herbicides that kill or prevent growth of broadleaf weeds. Such other herbicides should not substantially reduce the effect of the N-phenylamines on the grassy weeds and must not combine with the N-phenylamines to cause undesirable effects on the growth of crop plants. Therefore, according to a further aspect of the invention, a combination herbicidal composition for controlling both grassy and broadleaf weeds comprises a mixture of a N-phenylamine according to the invention and norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine or pyrazon, in a weight ratio to the N-phenylamine of from 4:1 to 1:12.

Norea, fluometuron, chloroxuron, diuron and linuron are all commercially available herbicides that are known to have some toxicity toward broadleaf weeds. They have not heretofore been used in combination with the substituted N-phenylamines according to the invention.

Norea is the common name for 3 - (3a, 4,5,6,7,7a - hexahydro - 4,7 - methanoindan - 5 - yl) - 1,1 - dimethyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 3,304,167, to Buntin *et al.* It is commercially available under the Herban trademark.

Fluometuron is the common name for N - (3 - trifluoromethylphenyl) - N',N' - dimethyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 3,134,665, to Martin *et al.* It is commercially available as Cotoran.

Chloroxuron is the common name for 3 - [p - (p - chloro - phenoxy)phenyl] 1,1 - dimethyl urea. This compound and a process for making it are disclosed in the U.S. Patent, No. 3,060,235, to Martin *et al.* It is commercially available under the registered Trade Mark "Tenoran."

Diuron is the common name for 3 - (3,4 - dichlorophenyl) - 1,1 - dimethyl urea. This

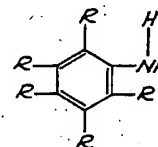
compound and its preparation are disclosed in the U.S. Patent, No. 2,655,445, to Todd. It is commercially available under the name of registered Trade Mark "Karmex."

Linuron is the common name for 3 - (3,4 - dichlorophenyl) - 1 - methoxy - 1 - methyl urea. This compound and its preparation are disclosed in the U.S. Patent, No. 2,960,534, to Scherer *et al.* It is commercially available under the name Lorox.

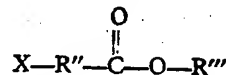
A fourth aspect of the invention, a process for controlling both grassy and broadleaf weeds, comprises applying to the habitat of the weeds an effective quantity of the said combination herbicidal composition.

The substituted N-phenylamines of this invention are brown, yellow-brown or yellow and are either liquid or solid at 20-25°C. Esters according to the invention are insoluble in water but they are soluble to an extent suitable for herbicidal uses in solvents; for example acetone and benzene. On the other hand, the acids, salts, amides and hydrazides according to the invention are soluble in water at least to the extent suitable for herbicidal uses.

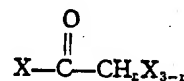
The N-phenylamines can be made by reacting in a liquid reaction medium containing a base, for example potassium hydroxide, the corresponding phenylamine:



with a haloalkanoic acid or ester of the formula:



in which X is halo and the group $-\text{CO}-\text{OR}'''$ is Q as defined above, to form the compounds of the class in which R' is hydrogen. These compounds are reacted with mono-, di- and trihaloacetylhalides of the formula



in which n is 0, 1 or 2, to form the remaining N-phenylamines of this invention.

The herbicidal compositions according to the invention are used by applying them in conventional ways to soil as well as to the foliage of weeds.

The rate of application of the compositions should be such as to provide an effective concentration of the phytotoxic material in the soil, on the weed foliage, or both in the soil and on the foliage, depending on the method

of application and what is desired.

In the case of these herbicidal compositions that are normally solid, the "application aid" material is generally an inert solid in a divided condition. Some embodiments of these compositions are granular, while others are dispersible powders or dusts. The granular compositions may be made by coating, impregnating or incorporating.

The coated granular compositions are made by dusting a wettable powder or ground powder of the phytotoxic material onto granular carrier material which either before or after the dusting has been mixed with a sticker.

Water, oils, alcohols, glycols, aqueous gums and waxes, including mixtures thereof, are used as stickers. Examples of granular carrier material include attaclay, corn cobs, vermiculite, walnut hulls and almost any granular mineral or organic material screened to the desired size. Generally the phytotoxic material is 2—20% by weight of the granular composition, the sticker is generally 5—40% by weight of the composition and the granular carrier material is generally 60—93% by weight of the composition.

The impregnated granular compositions are made by dissolving the phytotoxic material in a solvent or melting it, and then spraying or pouring the liquid so formed onto the granular carrier material. Solvent can be removed by evaporation, or permitted to remain. The phytotoxic material impregnates the particles of the granular carrier material. Examples of the granular carrier material include those just mentioned with respect to the coated type of granular composition. The phytotoxic mixture is generally 2—20% by weight of the composition, while the granular carrier material is generally 80—98% by weight of the composition.

To make the incorporated granular compositions, the phytotoxic mixture is mixed with an inert finely divided solid for example, clay, carbon or plaster of paris, and made into a mud with water or other inert evaporable liquid. The mud is then dried to a solid sheet or cake, broken up or comminuted, and screened to the desired particle size. In other embodiments, the mud is put into a granular pan and granules are formed therein with subsequent removal of the water or solvent. In still another procedure, the mud is extruded through a die into rods which are cut into small pieces. In the incorporated type of granular composition, the phytotoxic mixture generally is 2—50% by weight of the composition, and the solid carrier material is 50—98% by weight of the composition.

In all granular embodiments of the dispersible herbicidal compositions of this invention, various additives in minor concentrations relative to the carrier material also can be present.

In the powder or dust types of the dis-

persible solid herbicidal compositions of this invention, the carrier is usually a dispersible inert solid, for example clay. Other suitable dispersible solids are talc, attapulgit, pyrophyllite, diatomaceous earth, kaolin, aluminum magnesium silicate, montmorillonite, Fullers earth, and sawdust. If the solid dispersible compositions are air dispersible, they can be applied as dusts. If they are water dispersible they are usually referred to as "wettable powders". The water dispersible compositions preferably contain emulsifying material, for example a surfactant, at concentration sufficient to enable a suspension of the desired degree of stability to be formed when the composition is mixed with a suitable quantity of water. A typical dispersible solid composition of this invention generally comprises 10—80% by weight of phytotoxic mixture, 20—90% by weight of solid carrier material, and, when emulsifying material is present, 1—10% by weight of emulsifying material.

Other specific embodiments of the herbicidal composition of this invention comprise solutions of the phytotoxic mixture of this invention in inert, preferably volatile, solvents for the phytotoxic mixture. Such a solution, which can be regarded as a concentrate, typically comprises 10—50% by weight of phytotoxic mixture and 50—90% by weight of solvent. The solution can be applied as it is, or diluted with more solvent and applied, or, when one or more components of the phytotoxic mixture are water-insoluble, dispersed in water or water dispersed in it, and applied. Preferably, when it is intended that the solution of water-insoluble components be dispersed in water or water be dispersed in it, the mixture of solution and water also comprises emulsifying material at a concentration sufficient to enable a dispersion of the desired degree of stability to be formed. A typical emulsifying material concentration is 1—10% by weight of the concentrate. The water concentration is such that the phytotoxic mixture concentration is 0.5—10% by weight of the total composition.

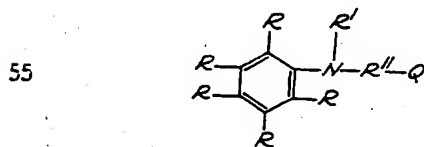
Examples of the surfactants employed in both the liquid and solid compositions of this invention comprise the well-known surface active agents of the anionic, cationic or non-ionic types and include alkali metal (sodium or potassium) oleates, amine salts of long chain fatty acids (oleates), sulfonated animal and vegetable oils (fish oils and castor oil), sulfonated petroleum oils, sulfonated acyclic hydrocarbons, sodium salts of lignin sulfonic acids, alkyl naphthalene sodium sulfonates, sodium lauryl sulfonate, disodium monolauryl phosphates, sorbitol laurate, pentaerythritol monostearate, glycerol monostearate, polyethylene oxides, ethylene oxide condensates of stearic acid, stearyl alcohol, stearyl amine, rosin amines and dehydroabietyl amine, lauryl amine salts, dehydroabietyl amine salts, lauryl

pyridinium bromide, stearyl trimethylammonium bromide, and cetyl dimethylbenzylammonium chloride. Still other examples are listed in "Detergents and Emulsifiers — 1968 Annual" by John W. McCutcheon.

In addition to the phytotoxic mixture and application aid material, some specific embodiments of the dispersible herbicidal composition of this invention comprise one or more other components, examples of which include plant growth regulators, insecticides, acaricides, fungicides, nematocides and plant nutrients.

For determining the specific chemical structures for the N-substituted N-phenylamines according to the invention, it may be noted that C_1-C_7 alkyl includes both straight and branched chain alkyl, examples of which include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl and pentyl. C_1-C_7 alkoxy encompasses both straight and branched chain alkoxy having 1—7 carbon atoms, examples of which include methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy and pentoxy. Halo includes fluoro, chloro, bromo and iodo. C_2-C_7 alkylene comprises both straight and branched chain alkylene having 1—7 carbon atoms, examples of which include ethylene, propylene, 1 - methylethylene, 2 - methylethylene, butylene, 1 - methylpropylene, 2 - methylpropylene, 3 - methylpropylene, 1,1 - dimethylethylene, 1,2 - dimethylethylene and 2,2 - dimethylethylene. C_2-C_7 alkylidene comprises both straight and branched chain alkylidenes having 2—7 carbon atoms, for example, ethylidene, propylidene, isopropylidene, butylidene, 1 - methylpropylidene, 2 - methylpropylidene, and 2,2 - dimethylethylene. C_2-C_7 alkylidene comprises both straight and branched chain alkylidenes having 2—7 carbon atoms, for example, ethylidene, propylidene, isopropylidene, butylidene, 1 - methylpropylidene and 2 - methylpropylidene. Examples of salts include ammonium salt, alkali metal salts (e.g. sodium and potassium), alkaline earth metal salts (e.g. calcium and magnesium) and amine salts (methylamine, diethylamine, tripropylamine and diphenylamine). Examples of C_1-C_7 alkanol esters include the methyl ester, ethyl ester, the propyl ester and the isopropyl ester. Aryl includes phenyl, tolyl and naphthyl.

A number of compounds covered by the generic formula



are shown for reference in the following list, wherein ϕ indicates a compound of Formula II:—

Compound No.	Name	
1	N - (p - chlorophenyl) - glycine ethyl ester	60
2	N - (m - chlorophenyl) - glycine ethyl ester	
3	N - (o - chlorophenyl) - glycine ethyl ester	65
4	N - phenylglycine ethyl ester	
5	N - (2,3 - dichlorophenyl) - glycine ethyl ester	
6	N - (3,4 - dichlorophenyl) - glycine ethyl ester	70
7	N - (2 - chloro - 4 - nitrophenyl) - glycine ethyl ester.	
8	N - (4 - chloro - 3 - nitrophenyl) - glycine ethyl ester	75
9	N - (2,4,5 - trichlorophenyl) - glycine ethyl ester	
10	N - chloroacetyl - N - (p - chlorophenyl) - glycine ethyl ester	80
11	N - chloroacetyl - N - (m - chlorophenyl) - glycine ethyl ester	
12	N - chloroacetyl - N - (o - chlorophenyl) - glycine ethyl ester	85
13	N - chloroacetyl - N - phenylglycine ethyl ester	
14	N - chloroacetyl - N - (2,3 - dichlorophenyl) - glycine ethyl ester	90
15	N - chloroacetyl - N - (3,4 - dichlorophenyl) - glycine ethyl ester	
16	N - dichloroacetyl - N - (p - chlorophenyl) - glycine ethyl ester	95
17	N - dichloroacetyl - N - (m - chlorophenyl) - glycine ethyl ester	100
18	N - dichloroacetyl - N - (o - chlorophenyl) - glycine ethyl ester	
19	N - dichloroacetyl - N - phenylglycine ethyl ester	105
20	N - dichloroacetyl - N - (2,3 - dichlorophenyl) - glycine ethyl ester	
21	N - dichloroacetyl - N - (3,4 - dichlorophenyl) - glycine ethyl ester	110
22	N - trichloroacetyl - N - (p - chlorophenyl) - glycine ethyl ester	
23	N - trichloroacetyl - N - (m - chlorophenyl) - glycine ethyl ester	115
24	N - trichloroacetyl - N - (o - chlorophenyl) - glycine ethyl ester	
25	N - trichloroacetyl - N - phenylglycine ethyl ester	120

Compound No.	Name	Compound No.	Name
26	N - trichloroacetyl - N - (2,3 - dichlorophenyl) - glycine ethyl ester	47	N - dichloroacetyl - N - (2,6 - dichlorophenyl) - glycine ethyl ester
27	N - trichloroacetyl - N - (3,4 - dichlorophenyl) - glycine ethyl ester	48	N - trichloroacetyl - N - (2,6 - dichlorophenyl) - glycine ethyl ester
28	N - chloroacetyl - N - (2 - chloro - 4 - nitrophenyl) - glycine ethyl ester	49	N - chloroacetyl - N - (4 - chloro - 2,6 - dinitrophenyl) - glycine ethyl ester
29	N - chloroacetyl - N - (4 - chloro - 3 - nitrophenyl) - glycine ethyl ester	50	N - trichloroacetyl - N - (4 - chloro - 2,6 - dinitrophenyl) - glycine ethyl ester
30	N - chloroacetyl - N - (2,4,5 - trichlorophenyl) - glycine ethyl ester	51	N - chloroacetyl - N - (2,6 - dichloro - 4 - nitrophenyl) - glycine ethyl ester
31	N - dichloroacetyl - N - (2 - chloro - 4 - nitrophenyl) - glycine ethyl ester	52	N - dichloroacetyl - N - (2,6 - dichloro - 4 - nitrophenyl) - glycine ethyl ester
32	N - dichloroacetyl - N - (4 - chloro - 3 - nitrophenyl) - glycine ethyl ester	53	N - trichloroacetyl - N - (2,6 - dichloro - 4 - nitrophenyl) - glycine ethyl ester
33	N - dichloroacetyl - N - (2,4,5 - trichlorophenyl) - glycine ethyl ester	54	N - (2,4 - dichlorophenyl) - glycine ethyl ester
34	N - trichloroacetyl - N - (2 - chloro - 4 - nitrophenyl) - glycine ethyl ester	55	N - chloroacetyl - N - (2,4 - dichlorophenyl) - glycine ethyl ester
35	N - trichloroacetyl - N - (4 - chloro - 3 - nitrophenyl) - glycine ethyl ester	56	N - dichloroacetyl - N - (2,4 - dichlorophenyl) - glycine ethyl ester
36	N - trichloroacetyl - N - (2,4,5 - trichlorophenyl) - glycine ethyl ester	57	N - trichloroacetyl - N - (2,4 - dichlorophenyl) - glycine ethyl ester
37φ	N - chloroacetyl - N - (2,6 - diethylphenyl) - glycine ethyl ester	58	N - (2,6 - diethylphenyl) - glycine ethyl ester
38	N - chloroacetyl - N - (3 - chloro - 2 - methoxyphenyl) - glycine ethyl ester	59	N - chloroacetyl - N - phenyl - alanine
39φ	N - dichloroacetyl - N - (2,6 - diethylphenyl) - glycine ethyl ester	60	N - bromoacetyl - N - phenyl - alanine
40	N - dichloroacetyl - N - (3 - chloro - 2 - methoxyphenyl) - glycine ethyl ester	61	4 - (N - chloroacetyl anilino) - butyramide
41φ	N - trichloroacetyl - N - (2,6 - diethylphenyl) - glycine ethyl ester	62φ	α - (N - chloroacetyl - 2',6' - diethylanilino) - acetylhydrazine
42	N - trichloroacetyl - N - (3 - chloro - 2 - methoxyphenyl) - glycine ethyl ester	63	4 - (N - trichloroacetyl - 2',6' - dichloroanilino) - butyric acid sodium salt
43	N - (2,6 - dichlorophenyl) - glycine ethyl ester	64	4 - (N - trichloroacetyl - 3',4' - dichloroanilino) - crotyric acid
44	N - (4 - chloro - 2,6 - dinitrophenyl) - glycine ethyl ester	65	2 - [4 - (2',4' - dichloroanilino) - butyryl] - 1 - phenyl - hydrazine
45	N - (2,6 - dichloro - 4 - nitrophenyl) - glycine ethyl ester	66	N - chloroacetyl - N - (2',4',5' - trichlorophenyl) - alanine
46	N - chloroacetyl - N - (2,6 - dichlorophenyl) - glycine ethyl ester	67	4 - (N - trichloroacetyl anilino) - butyric acid ammonium salt
		68	N - chloroacetyl - N - (m - trifluoromethylphenyl) - glycine ethyl ester
		69	N - trichloroacetyl - N - (m - trifluoromethylphenyl) - alanine ethyl ester

Compound No.	Name	Compound No.	Name	
70	N - (p - trifluoromethylphenyl) - glycine	92	N - bromoacetyl - N - (2,6 - diethylphenyl) - glycine ammonium salt	65
5 71φ	N - chloroacetyl - N - (2,6 - diethylphenyl) - alanine ethyl ester	93φ	N - bromoacetyl - N - (2,6 - diethylphenyl) - glycine ethyl ester	70
72φ	N - carbethoxyethyl - N - chloroacetyl - 2,6 - diethylalanine			
10 73φ	N - chloroacetyl - N - (2 - methyl - 6 - ethylphenyl) - alanine ethyl ester	In the following preparation procedures and examples, all percentages are by weight unless otherwise indicated, all parts by weight are indicated by "w", all parts by volume are indicated by "v", and each part by weight (w) bears the same relationship to each part by volume (v) as the kilogram does to the liter.		
74φ	N - carbethoxyethyl - N - chloroacetyl - 2 - methyl - 6 - ethyl - aniline			75
15 75	N - chloroacetyl - N - (2,6 - dimethylphenyl) - glycine	Preparation Procedure I.		
76	N - chloroacetyl - N - (2,6 - dimethylphenyl) - glycine sodium salt		N - (2,6 - diethylphenyl) - glycine ethyl ester, one of the N - substituted N - phenylamines useful according to the invention, can be made as follows:	80
20 77	N - chloroacetyl - N - (2,6 - dimethylphenyl) - glycine ammonium salt		Ethyl bromoacetate (480 w) is added dropwise to a stirred mixture of 2,6 - diethylaniline (429 w), potassium hydroxide (161 w) and dimethylformamide (1500 v). During the addition of ethyl bromoacetate, the temperature of the reaction mixture typically rises slightly. After addition is complete, the mixture is stirred at 90—110°C. for one hour. During this period of time the potassium hydroxide dissolves and a white precipitate slowly forms. The reaction mixture is cooled to 20—25°C., poured into water (2000 v) and extracted with diethyl ether (700 v) three times. The ether extracts are combined, washed with water, an aqueous solution of hydrochloric acid (10%), an aqueous solution of sodium bicarbonate (5%), and water, and then dried. The diethyl ether is removed by evaporation under reduced pressure. The residue (426.8) is typically a red oil. It consists essentially of N - (2,6 - diethylphenyl) - glycine ethyl ester.	85
25 78φ	N - chloroacetyl - N - (2,6 - dimethylphenyl) - glycine ethyl ester			
79	N - chloroacetyl - N - (2,6 - diethylphenyl) - glycine			90
30 80	N - chloroacetyl - N - (2,6 - diethylphenyl) - glycine sodium salt			
81	N - chloroacetyl - N - (2,6 - diethylphenyl) - glycine ammonium salt			95
35 82	N - chloroacetyl - N - (2 - methyl - 6 - ethylphenyl) - glycine			
83	N - chloroacetyl - N - (2 - methyl - 6 - ethylphenyl) - glycine sodium salt			100
40 84	N - chloroacetyl - N - (2 - methyl - 6 - ethylphenyl) - glycine ammonium salt			
45 85φ	N - chloroacetyl - N - (2 - methyl - 6 - ethylphenyl) - glycine ethyl ester			105
86	N - chloroacetyl - N - (2 - chloro - 6 - methylphenyl) - glycine			
50 87	N - chloroacetyl - N - (2 - chloro - 6 - methylphenyl) - glycine sodium salt			110
88	N - chloroacetyl - N - (2 - chloro - 6 - methylphenyl) - glycine ammonium salt			
55 89	N - chloroacetyl - N - (2 - chloro - 6 - methylphenyl) - glycine ethyl ester			115
90	N - bromoacetyl - N - (2,6 - diethylphenyl) - glycine			
60 91	N - bromoacetyl - N - (2,6 - diethylphenyl) - glycine sodium salt			120

Preparation Procedure II.

N - chloroacetyl - N - (2,6 - diethylphenyl) - glycine ethyl ester, another N - substituted N - phenylamine of this invention, can be made as follows:

To a stirred solution of 2,6 - diethylphenylglycine ethyl ester (31.5 w), made as in Example 1, in benzene (2.5 v) is added dropwise chloroacetyl chloride (306 w) followed by pyridine (196 w). During the additions the temperature of the reaction mixture typically rises from 20—25°C. to about 70°C. After the additions are complete, the resulting

reaction mixture is stirred at 70—80°C. for 3 hours, cooled to 20—25°C., and filtered. The filtrate is washed with the water, an aqueous solution of hydrochloric acid (10%), an aqueous solution of sodium bicarbonate (5%), and water, and then dried. The benzene is removed by evaporation under reduced pressure. The residue (711.0 w), the desired product, is typically a red oil which crystallizes on standing. A typical analysis of the product is: N=4.4%, Cl=11.9%; (calculated: N=4.4%, Cl=11.3%). The product consists essentially of N - chloroacetyl - (2,6 - diethyl - phenyl) - glycine ethyl ester.

In similar fashion the other N - phenylamines of this invention in which R' is mono-, di- and trihaloacetyl are made from the corresponding compounds of this invention in which R' is H, and the corresponding mono-, di- and trihaloacetyl halides.

Examples 1—75.

The general formulation of the compositions are:

	Components	Concentration
25	Phytotoxic material	1 w
	Poly(oxyethylene)sorbitan mono-laurate in which the average oxyethylene content is 20 mole %	1 v
30	Toluene	1 v

The phytotoxic material in this example contains the compounds listed on pages 9 to 14. The herbicidal utilities of those compounds are illustrated by the test data set forth in the following table. These test data were obtained in actual routine greenhouse testing of products consisting essentially of the compounds of this invention. For each numbered compound, a water emulsifiable concentrate was made by dissolving a sample

(15 w) of the product in acetone (400 v) and then admixing a commercially available emulsifier [a blend of polyoxyethylene (20) sorbitan monooleate in which the average oxyethylene content is about 20 mole %, mono, and di-glycerides of fat forming fatty acids, and an antioxidant mixture consisting essentially of butylated hydroxyanisole, butylated hydroxy-toluene, citric acid and propylene glycol] (20 v). The liquid concentrate was then dispersed in water and the resulting emulsion applied by spraying at standard test rates.

In the post-emergence (foliage spray) test, the emulsion was sprayed at rates of 1 and 10 pounds of test product per acre on growing plants at the first true leaf stage. The plants were millet, corn, mustard, cotton, tomato and marigold. After a prescribed interval of time during which the sprayed plants as well as unsprayed plants of the same age were subjected to favorable growing conditions in a greenhouse, the sprayed plants were inspected for injury and kill, compared with the unsprayed plants, and the extent of injury or kill rated on a scale of 0—10 with 0 being no injury or kill and 10 being 100% injury or kill.

In the pre-emergence (soil germination) test the emulsion was sprayed at rates of 2 and 20 pounds of test product per acre on soil freshly seeded with the seeds of soybean, millet, corn, mustard and cotton. After subjecting the sprayed seeded soil as well as unsprayed soil freshly seeded with these seeds to controlled favorable growing conditions in a greenhouse for a time sufficient for germination and plant growth, the containers of the soil were inspected for plant growth and injury, and compared to the containers of unsprayed seeded soil. The extent of injury or kill was rated on a scale of 0—10 with 0 being no injury or kill and 10 being 100% injury or kill.

TABLE I

Compound Ex. No.	Foliage Spray Test						Soil Germination Test				
	Rate			Mari-			Rate	Soy-			
	Millet	Corn	Mustard	Cotton	Tomato	gold		bean	Millet	Corn	Mustard Cotton
1	1	2	0	2	6	5	0	2	10	2	0
2	10	8	2	9+	10	10	10	20	10	10	0
3	1	0	0	3	2	0	0	2	7	0	0
4	10	2	1+	8	1	2	2	20	10	10	0
5	1	0	0	0	0	1	0	2	2	0	0
6	10	3	10	5	2	4	0	20	10	0	0
7	1	0	0	0	0	0	0	2	0	0	0
8	10	3	2	4	3	1	2	20	10	4	0
9	1	0	2	0	1	0	0	2	0	0	0
10	10	6	9	6	4	4	0	20	10	6	1
11	1	0	0	7	5	5	6	2	10	3	0
12	10	5	6	9	10	9	9	20	10	8	5
13	1	3	5	0	4	1	0	2	0	0	0
14	10	10	10	10	10	10	6	20	0	5	0
15	1	0	0	6	2	0	5	2	0	0	0
16	10	9	9	10	8	10	10	20	10	9	2
17	1	5	0	5	2	7	2	2	4	0	0
18	10	8	10	10	10	10	10	20	10	10	2
19	1	0	0	0	0	0	0	2	1	0	0
20	10	8	7	9	6	10	9	20	9	8	6
21	1	2	2	0	2	1	1	2	0	0	0
22	10	10	10	9	7	10	9	20	9	9	0
23	1	2	0	2	0	0	0	2	0	0	1
24	10	9	8	8	8	10	9	2	0	0	0
25	1	0	0	0	0	1	0	20	1	10	3
26	10	9	10	9	5	10	6	2	0	0	0
27	1	0	1	0	0	0	0	2	0	0	0
28	10	8	6	9	9	9	1	20	2	9	0
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TABLE I (Cont'd)

Compound Ex. No.	Foliage Spray Test					Soil Germination Test				
	Rate	Millet	Corn	Mustard	Cotton	Mari- Tomato gold	Rate	Soy- bean	Millet	Corn
									Mustard	Cotton
28	1 10	0 10	1 10	1 10	1 9	0 10	2 20	2 8	0 9	0 3
29	1 10	0 9	0 10	1 10	0 3	0 10	2 20	0 4	0 5	0 0
30	1 10	4 8	0 10	3 9	2 9	0 8	2 20	1 8	2 4	0 7
31	1 10	0 10	0 10	0 10	0 5	0 10	2 20	0 0	0 0	0 7
32	1 10	4 9	0 10	0 8	0 5	0 8	2 20	0 9	0 4	1 7
33	1 10	2 8	2 10	1 9	2 7	0 10	2 20	0 6	0 2	2 3
34	1 10	3 10	8 10	5 10	2 10	0 10	2 20	6 8	9 10	0 2
35	1 10	1 9	1 10	2 10	2 5	0 8	2 20	2 9	8 10	1 4
36	1 10	8 9	4 9	5 10	4 8	1 8	2 20	0 9	0 10	0 6
37	1 10	1 9	0 9	0 9	2 9	2 5	2 20	7 6	9 7	1 0
38	1 10	0 6	0 10	2 7	0 5	0 4	2 20	6 7	9 10	0 0
39	1 10	0 5	2 8	0 9	0 5	0 3	2 20	5 3	10 10	0 4
40	1 10	0 8	0 8	0 8	2 8	0 3	2 20	0 10	0 4	0 1
41	1 10	0 4	2 9	1 5	0+ 1	2 10	2 20	0 4	0 2	1 0
42	1 10	0 6	0 10	0 6	0 2	0 6	2 20	2 9	3 10	0 4

TABLE I (Cont'd)

Compound Ex. No.	Foliage Spray Test					Soil Germination Test							
	Mari-					Soy- bean	Rate						
	Rate	Millet	Corn	Mustard	Cotton		Tomato	gold	Millet	Corn	Mustard	Cotton	
56	1 10	2 10	3 10	1 10	5 10	0 10	2 10	2 20	3 10	0 5	0 2	1 5	0 0
57	1 10	8 10	6 10	2 10	6 10	9 10	3 10	2 20	4 10	10 10	3 10	1 8	0 3
71	1 10	9 10	2 10	9 10	1 9	4 8	2 6	2 20	6 10	10 10	9 10	8 10	0 10
72	1 10	5 10	2 8	2 10	0 6	3 6	0 4	2 20	2 7	10 10	9 10	0 9	0 1
73	1 10	0 6	2 10	0 7	0 3	0 0	0 0	2 20	10 10	9 10	0 0	0 7	0 3
74	1 10	3 10	3 10	1 10	0 9	2 8	0 7	2 20	0 9	10 10	10 10	1 10	4 5
75	1 10	5 10	2 10	1 10	0 4	1 8	2 6	2 20	0 9	10 10	8 10	9 10	1 3

Examples 76—82.

These examples illustrate specific embodiments of the combined herbicidal compositions of this invention.

The general formulation of these embodiments was the same as for Examples 1—75.

Each combined herbicidal composition was made by mixing the components at 20—25°C. to produce a phytotoxic mixture at whatever concentration was desired. The mixture was

sprayed over the area to be treated at the desired rate of application.

The components of the phytotoxic mixture in each example, relative weight ratio of the components, the crop or crops in which each specific composition is particularly useful, time of application (Pre=pre-emergence; Post=post-emergence), and suggested rates of application, based on the phytotoxic mixture, are set forth in the following Table II.

15

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TABLE II

Ex. No.	Components of Phytotoxic Mixture	Weight Ratio of Components	Crops	Time of Application	Weeds	Rate of Application (lbs./acre)
76	Product of Preparation Procedure II Norea	1:1-2:1	Barley Corn Cotton Peanuts Sorghum Soybeans Peas Snap beans Wheat	Pre	Downeybrome grass Foxtail grass Pigweed Wild oats Rye Grass Carpetweed Barnyard grass Crabgrass Mustard Coffee weed Velvet leaf Spurge Purslane	3/4 - 4
77	Product of Preparation Procedure II Fluometuron	1:1-2	Cotton Peas Peanuts	Pre	Foxtail Barnyard grass Crabgrass Wild oats Mustard Coffee weed Velvet leaf Teaweed Annual Morning Glory Pigweed Spurge Purslane	2-2
78	Product of Preparation Procedure II Cloroxuron	1:1-2:1	Soybeans	Post (Early when grasses have 1-2 leaves and height of 1 inch)	Crabgrass Green foxtail Barnyard grass Pigweed Mustard	2-3

TABLE II (Cont'd)

Ex. No.	Components of Phytotoxic Mixture	Weight Ratio of Components	Crops	Time of Application	Weeds	Rate of Application (lbs./acre)
79	Product of Preparation Procedure II Diuron	2:1-1:2	Wheat Cotton Soybeans Corn	Pre	Wild Oats Crabgrass Barnyard grass Pigweed Lambs quarter Rye grass Downeybrome grass Teaweed	3/4 -2
80	Product of Preparation Procedure II Linuron	2:1-1:2	Wheat Cotton Soybeans Corn	Pre	Velvet leaf Curled mustard Coffee weed Jimson weed Foxtail Rye grass Downeybrome grass	3/4 - 1-1/2
	Product of Preparation Procedure II Fenuron	0.4:1-1:2:1	Corn Cotton Soybeans	Pre	Crabgrass Foxtail Barnyard grass Teaweed Velvet leaf Pigweed Lambs Quarter Curled mustard Morning glory	1/2 - 1
81	Product of Preparation Procedure II Atrazine	12:1-1:1	Corn Sorghum	Post	German millet Crabgrass Green foxtail Barnyard grass Pigweed Mustard	1/2 - 3

TABLE II (Cont'd)

Ex. No.	Components of Phytotoxic Mixture	Weight Ratio of Components	Crops	Time of Application	Weeds	Rate of Application (lbs./acre)
82	Product of Preparation Procedure II Pyrazon	1:1-1:4	Peas Red beets Sugar beets	Pre & Post	Crabgrass Green foxtail Barnyard grass Pigweed Mustard Jimson weed Velvet leaf Ragweed	3 - 6

Typical results obtained in the practice of this invention are exemplified by the following tabulated data which are the best data so far obtained in the actual testing of various embodiments of a composition of this invention. These data were obtained in standard greenhouse tests and in field tests. The results of these tests are in most instances expressed as % reduction in growth in the case of the pre-emergence tests, and % kill or injury in the case of post-emergence tests. In all of these tests the results were determined by comparing treated areas with untreated control areas in the pre-emergence tests, and treated plants with untreated control plants in the post-emergence tests. In the following tables the legend "lb/A.a.:" means pounds of active agent per acre.

20 Synergism was deemed to be present when the observed result was substantially greater

than the expected result which was calculated according to the equation:

$$E = x + y - \frac{xy}{100}$$

in which x is the % reduction of growth or % kill or injury by herbicide A at p pounds per acre, y is the % reduction of growth or % kill or injury by herbicide B at q pounds per acre, and E is the expected % reduction of growth or % kill or injury by herbicides A and B at p + q pounds per acre. The basis and logic of this equation are discussed in Weeds, 15, pages 20-22.

Table III presents pre-emergence data obtained in field tests of N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, norec, fluometuron, mixtures of the ester and norec, and mixtures of the ester and fluometuron.

TABLE III

Phytotoxic Material	Rate (lb/A.a.i.)	Fox- tail	Barn- yard grass	Crab grass	Wild Oats	Average Grasses	Mus- tard	Coffee weed	Vel- vet leaf	Tea weed
N-Chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	94	99	99	65	89	7	7	12	0
	2.0	99	100	100	72	93	6	7	20	7
Norea	1.5	70	71	97	62	75	77	66	85	0
Ester + Norea	1.0 + 1.5	99	99	100	90*	97	90*	70	90	30*
	2.0 + 1.5	96	100	100	90*	96	88*	33	73	38*
Fluometuron	1.2	87	75	97	90	87	100	94	92	100
Ester + Fluometuron	1.0 + 1.2	100	97	100	95	98	100	99	96	100

* Synergistic result

TABLE III (Cont'd)

Phytotoxic Material	Rate (lb./A.a.i.)	Sweet peas	Wheat	Snap beans	Rice	Cotton	Soy- beans	Sorghum	Corn	Sugar beets
N-Chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1.0	5	5	0	25	5	0	4	5	0
	2.0	11	11	1	41	0	0	24	0	6
Norea	1.5	12	31	5	54	7	0	0	4	80
Ester + Norea	1.0 + 1.5	7	30	30	74	0	14	4	11	90
	2.0 + 1.5	10	45	27	68	1	2	19	7	98
Fluometuron	1.2	26	55	82	82	6	37	26	10	100
Ester + Fluometuron	1.0 + 1.2	22	65	83	89	11	49	45	40	100

TABLE III (Cont'd)

Phytotoxic Material	Rate (lb./A.a.i.)	Annual Morning Glory	Pig- weed	Spurge	Cockle- bur	Purs- lane	Av. Broad leaf	Cu- cum- ber	Al- falfa	Pea- nuts
N-Chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	1.0	5	95	71	5	90	32	10	0	4
	2.0	2	100	89	7	100	38	30	10	7
Norea	1.5	25	91	74	12	100	59	82	77	2
Ester + Norea	1.0 + 1.5	4	100	95	32	100	68	75	76	0
	2.0 + 1.5	15	99	92	32	100	63	60	75	2
Fluometuron	1.2	75	100	97	19	100	86	97	100	50
Ester + Fluometuron	1.0 + 1.2	81	100	99	22	100	89	77	100	26

Table IV presents pre-emergence data obtained in greenhouse tests of N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, norea and mixtures of the two relative to weed control and wheat tolerance.

TABLE IV

Phytotoxic Material	Rate lb/A.a.i.	% Weed Control					% Wheat Injury
		Curled Mustard	German Millet	Barn- yard Grass	Corn Cockle	Downey- brome Grass	
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	0.5	0	97	97	0	35	0
Norea	0.5	0	45	80	0	10	16
	1.0	60	97	100	15	60	38
Ester + Norea	0.5 + 0.5	40*	100	97	45*	85*	16
	0.5 + 1.0	95*	100	100	45*	97*	0

*Synergistic result

Table V presents pre-emergence data obtained in greenhouse tests of N - chloroacetyl-N - (2,6 - diethylphenyl) glycine ethyl ester, norea, diuron, linuron, mixtures of the ester and diuron, and mixtures of the ester and linuron on ryegrass and downy brome grass.

TABLE V

Phytotoxic Material	Rate lb/A.a.i.	% Control	
		Ryegrass	Downeybrome
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	3/8	0	10
	3/4	70	82
Norea	3/8	50	43
	3/4	80	90
Ester + Norea	3/8 + 3/8	80*	58*
	3/4 + 3/8	98*	72
	3/8 + 3/4	93*	90
	3/4 + 3/4	95	75
Diuron	3/8	20	15
	3/4	85	28
Ester + Diuron	3/8 + 3/8	17	33*
	3/4 + 3/8	83	70
	3/8 + 3/4	57	75*
	3/4 + 3/4	93	80
Linuron	3/8	0	3
	3/4	20	20
Ester + Linuron	3/8 + 3/8	57*	55*
	3/4 + 3/8	87*	62
	3/8 + 3/4	63*	72*
	3/4 + 3/4	85*	60

*Synergistic result

5 Table VI presents data obtained in post-emergence field tests in soybeans of N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, chloroxuron, and mixtures of these two compounds. In this table EP stands for early post-emergence application, that is, when grasses have 1—2 leaves and are 1 inch tall, while P stands for post-emergence application when grasses have 3—4 leaves and are 2—3 inches tall. 10

TABLE VI

Phytotoxic Material	Rate lb/A.a./i.	Time of Appli- cation	% Weed Control					% Soybean Injury
			Crab- Grass	Green Fox- tail	Barn- yard Grass	Pig- weed	Mustard	
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	EP	25	25	0	18	0	0
	2.0		38	62	72	30	0	0
Chloroxuron	1.0	EP	60	92	85	100	100	35
	2.0		96	94	97	99	100	80
Ester + Chloroxuron	1.0 + 1.0	EP	80*	88	80	100	100	25
	2.0 + 1.0		98*	90	98	100	100	48
Ester	1.0	P	0	10	28	35	18	0
	2.0	P	30	5	42	75	0	0
Chloroxuron	1.0	P	42	45	55	100	98	65
	2.0		82	58	52	100	100	42
Ester + Chloroxuron	1.0 + 1.0	P	62*	75*	78*	100	100	48
	2.0 + 1.0		82*	78*	85*	100	100	48

*Synergistic Result

Tables VII and VIII set forth greenhouse data obtained in the pre-emergence testing of N - chloroacetyl - N - (2,6 - diethyl-phenyl)glycine ethyl ester, linuron and mixtures of these two compounds. These data are based on a scale of 0-10 with 0 being no kill or injury or inhibition of growth and 10 being 100% kill or injury or inhibition of growth.

TABLE VII

Phytotoxic Material	Rate lb/A.a.i.	Barnyard Grass	Crab- grass	Morning Glory	Tea Weed	Velvet Leaf	Mari- golds	Curled Mustard
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	3/8	10	8	0	6	0	4	0
Linuron	3/8 3/4	3 8	3 10	1 5	1 10	10 10	2 6	10 10
Ester + Linuron	3/8 + 3/8 3/8 + 3/4	10 10	9 10	0 1	8* 10	10 10	3 4	10 10

TABLE VII (Cont'd)

Phytotoxic Material	lb/A.a.i.	Coffee- weed	Jimson Weed	Sorghum	Soybeans	Cotton
N-chloroacetyl-N- (2,6-diethylphenyl) glycine ethyl ester	3/8	2	2	3	0	2
Linuron	3/8 3/4	10 10	7 10	1 0	0 0	0 2
Ester + Linuron	3/8 + 3/8 3/8 + 3/4	8 10	7 8	6 9	0 0	2 2

*Synergistic result

TABLE VIII

Phytotoxic Material	Rate lb/A.a.i.	Soy- beans	Cotton	Sorghum	Corn	Morning Glory	Tea- weed	Pigweed
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1/2	0	3.0	5.5	2.0	0	5.0	8.5
Linuron	1/4 1/2	2.5 0	4.0 0	2.5 1.5	0 0	0 0	3.0 10.0	10.0 10.0
Ester + Linuron	1/2 + 1/4 1/2 + 1/2	5.5 0	2.5 1.0	7.5 5.0	0 1.5	1.5 1.5	1.5 9.5	10.0 10.0

TABLE VIII (Cont'd)

Phytotoxic Material	Rate lb/A.a.i.	Barnyard Grass	Foxtail	Velvet Leaf	Curled Mustard	Wild Oats
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1/2	10.0	9.5	4.0	2.5	3.5
Linuron	1/4 1/2	0 3.0	5.0 7.0	7.0 10.0	0 8.0	0 1.5
Ester + Linuron	1/2 + 1/4 1/2 + 1/2	10.0 10.0	10.0 10.0	6.5 9.5	7.0 8.5	10.0* 9.0*

*Synergistic result

Table IX reports greenhouse data obtained in pre-emergence testing of N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, diuron, linuron, mixtures of the ester and diuron, and mixtures of the ester and

linuron. These data are reported on a scale of 0-10 with 0 being no kill, injury or inhibition of growth and 10 being 100% kill, injury or inhibition of growth.

TABLE IX

Phytotoxic Material	Rate lb/A.a.i.	Wild Downey- Oats			Crab- grass		Barn- yard grass		Pig- weed		Lambs Al- Quar- ter		Cot- ton		Soy- beans		Sugar Beets	
		Wheat	9	4	10	5	10	5	3	5	0	0	0	0	0	0	0	0
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1/2	0	3	4	2	5	10	5	0	10	7	3	0	0	0	0	0	0
Diuron	1/4 1/2	5	5	1	10	5	10	5	10	10	10	4	0	0	0	0	0	8
Ester + Diuron	1/2 + 1/4 1/2 + 1/2	0	10	5	10	10	10	10	10	10	10*	10*	0	0	-	2	7	8
Linuron	1/4 1/2	0	0	3	9	9	9	0	9	10	10	5	0	0	0	0	7	8
Ester + Linuron	1/2 + 1/4 1/2 + 1/2	3	10	0	10	10	10	10	10	10	10	10*	0	0	3	9	9	9

*Synergistic result

Table X gives greenhouse data obtained in the pre-emergence testing of N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, fenuron, and mixtures of these two com-

pounds. The data in this table are based on a scale of 0-10 with 0 being no injury or kill or inhibition of growth, and 10 being 100% injury or kill or inhibition of growth.

TABLE X

Phytotoxic Material	Rate Lb/A.a.i.	Corn	Cotton	Soy beans	Crab- grass	Fox- tail	Barnyard Grass	Tea weed	Velvet leaf
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	3/8	0	0	0	7	10	9	1	0
Fenuron	0.15	0	0	0	1	1	2	8	10
	0.30	0	0	3	6	5	6	10	10
	0.45	2	1	4	7	6	6	9	10
Ester + Fenuron	3/8 + 0.15	0	0	3	8	10	9+	8	10
	3/8 + 0.30	3	1	2	9	10	9+	10	10
	3/8 + 0.45	4	1	6	10	10	9+	10	10

TABLE X (Cont'd)

Phytotoxic Material	Rate Lb/A.a.i.	Pigweed	Lambs Quarter	Curled Mustard	Morning Glory
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	3/8	8	0	0	0
Fenuron	0.15	9	9	10	6
	0.30	9+	10	9+	8
	0.45	10	9+	10	8
Ester + Fenuron	3/8 + 0.15	10	9+	10	1
	3/8 + 0.30	10	9+	10	8
	3/8 + 0.45	10	9+	10	9

In Table XII are set forth post-emergence data obtained in the greenhouse testing of N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester, atrazine and mixtures of the two compounds for the control of German Millet.

TABLE XI

<u>Phytotoxic Material</u>	<u>Rate (lb./A.a.i.)</u>	<u>Test #1</u>	<u>Test #2</u>
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1/2	20	26
	3/4	61	38
Atrazine	1/16	18	19
	1/8	74	50
Ester + Atrazine	1/2 + 1/16	75*	79*
	3/4 + 1/16	83*	77*
	1/2 + 1/8	85*	90*
	3/4 + 1/8	88	95*

*Synergistic result

In Table XII are set forth post-emergence data obtained in field testing N - chloroacetyl - N - (2,6 - diethylphenyl) glycine ethyl ester, atrazine and mixtures of these two compounds for weed control in grain sorghum. 5

In the table EP means early post-emergence application when the grasses have 1—2 leaves and are 1 inch tall, while P represents post-emergence application when the grasses have 3—4 leaves and are 2—3 inches tall. 10

TABLE XII

Phytotoxic Material	Rate (lb/A.a.i.)	Time of Appln.	% Weed Control				% Sorghum Injury
			Crab- grass	Green Foxtail	Barnyard Grass	Pig- weed	Mustard
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0	EP	25	25	0	18	0
	2.0		38	62	72	30	0
Atrazine	1.0	EP	48	85	68	100	100
Ester + Atrazine	1.0 + 1.0	EP	90*	99*	98*	100	100
	2.0 + 1.0	EP	100*	99*	100*	100	100
Ester	1.0	P	0	10	28	35	18
	2.0	P	30	5	42	75	0
Atrazine	0.5	P	65	42	48	100	100
	1.0	P	85	82	80	100	100
Ester + Atrazine	1.0 + 0.5	P	88*	82*	62	100	100
	2.0 + 0.5	P	92*	88*	96*	100	99
	1.0 + 1.0	P	84	65	90*	100	100
	2.0 + 1.0	P	98*	98*	99*	100	100

*Synergistic result

Table XIII presents results of pre-emergence field testing of N - chloroacetyl - N - (2,6 - diethylphenyl)glycine ethyl ester, pyrazon and mixtures of the two compounds for weed control in peas and red beets.

TABLE XIII

Phytotoxic Material	Rate lb/A.a.i.	% Weed Control				% Crop Injury	
		Annual Grasses	Lambs- quarter	Jimson Weed	Velvet Leaf	Rag- weed	Pigs- weed
N-chloroacetyl-N-(2,6-diethylphenyl)glycine ethyl ester	1.0	98	0	0	-	0	0
	2.0	100	20	0	-	0	13
Pyrazon	2.0	75	100	67	100	100	0
	4.0	87	100	98	100	100	13
Ester + Pyrazon	1.0 + 2.0	52	85	-	0	58	5
	1.0 + 4.0	96	98	100	100	100	35
	2.0 + 2.0	94	88	100	100	100	37
							20

*Synergistic result

control in sugar beets. In the table "Pre" means pre-emergence application and "Post" means post-emergence application.

Table XIV contains data obtained in the field testing of N - chloroacetyl - N - (2,6 - diethylphenyl)glycine ethyl ester, pyrazon and mixtures of the two compounds for weed

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TABLE XIV

Phytotoxic Material	Rate lb/A.a.i.	Time of Appln.	% Weed Control			% Injury Sugar beets
			Lambs- quarter	Rag- weed	Annual Grasses	
N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester	1.0 2.0 4.0	Pre Pre Pre	25 12 0	0 0 0	99 100 100	0 0 0
Pyrazon	4.0	Pre	99	100	99	0
Ester + Pyrazon	1.0 + 4.0 2.0 + 4.0	Pre Pre	97 98	100 96	99 99	3 5
Ester	1.0 2.0 4.0	Post Post Post	7 0 0	0 0 0	100 100 100	0 0 0
Pyrazon	4.0	Post	88	100	86	0
Ester + Pyrazon	2.0 + 2.0 2.0 + 4.0	Post Post	98 98*	100 100	100 100	0 0

*Synergistic result

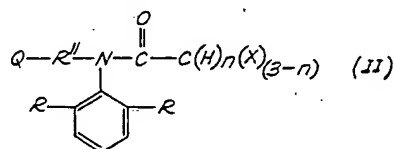
From the data of the foregoing tables it can be seen that the various embodiments of the phytotoxic material of this invention are effective against a number of both grassy weeds and broadleaf weeds while being tolerated by a number of crops. Moreover, these embodiments have synergistic phytotoxic effects on a variety of weeds.

10 The expression "consisting essentially of"

as used in this specification excludes and unspecified substance at a concentration sufficient to substantially adversely affect the essential properties and characteristics of the composition of matter being defined, while permitting the presence of one or more unspecified substances at concentrations insufficient to substantially adversely affect said essential properties and characteristics.

WHAT WE CLAIM IS:—

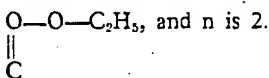
1. Compounds of the formula



in which each R, which can be the same

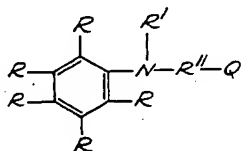
15

C_2H_5 , R'' is CH_2 , Q is



3. A herbicidal composition comprising application aid material and an effective quantity of phytotoxic material, wherein the phytotoxic material comprises an aromatic amine of the formula

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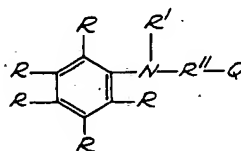
in which each R is hydrogen, halo, nitro, trihalomethyl, C_1-C_7 alkyl or C_1-C_7 alkoxy, R' is mono-, di- or trihaloacetyl, R'' is C_1-C_7 alkylene or C_2-C_7 alkylidene, and Q is carboxyl, a carboxyl salt, a C_1-C_7 alkanol ester of carboxyl, an amide, a mono- or di-substituted amide in which the substituents are C_1-C_7 alkyl or aryl radicals, a carbonylhydrazide radical or a 1-substituted carbonylhydrazide in which the substituent is C_1-C_7 alkyl or aryl.

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4. A herbicidal composition comprising application aid material and an effective quantity of phytotoxic material, wherein the phytotoxic material comprises an aromatic amine of the formula

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in which each R is hydrogen, halo, nitro, trihalomethyl, C_1-C_7 alkyl or C_1-C_7 alkoxy, R' is hydrogen, R'' is C_1-C_7 alkylene or C_2-C_7 alkylidene, and Q is carboxyl, a carboxyl salt, a C_1-C_7 alkanol ester of carboxyl.

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5. A composition according to Claim 3 or 4, wherein said aromatic amine is a com-

as or different from the other, is C_1-C_7 alkyl, R'' is C_1-C_7 alkylene or C_2-C_7 alkylidene, and Q is C_1-C_7 alkoxy, carbonyl, amide, mono- or di-substituted amide in which the substituents are C_1-C_7 alkyl or aryl, carbonylhydrazide and 1-substituted carbonylhydrazide in which the substituents are C_1-C_7 alkyl or aryl, X is halo, and n is 0, 1 or 2.

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2. A compounds according to Claim 1, in which each R is

pound as claimed in Claim 1 or 2.

6. A composition according to Claim 3, 4 or 5, also including a complementary herbicidal compound which is norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine or pyrazon in a weight ratio to the N-phenylamine of from 4:1 to 1:12.

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7. A process for the control of undesirable plants which comprises applying to the habitat of said plants an effective quantity of a compound defined in Claim 1, 2, 3 or 4.

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8. A process according to Claim 7, comprising also applying an effective quantity of a complementary herbicidal compound which is norea, fluometuron, chloroxuron, diuron, linuron, fenuron, atrazine or pyrazon to control grassy and broadleaf weeds.

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9. A process according to Claim 8, characterised by a weight ratio of complementary compound to aromatic amine compound of from 4:1 to 1:12.

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10. A process according to Claim 7 or 8, characterised by an application by an application rate of each compound of from 1/7 to 5 pounds per acre.

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11. A process according to any one of Claims 8 to 10, wherein the aromatic amine compound and the complementary compound are synergistically phytotoxic to at least one of said weeds.

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12. A process according to any one of Claims 7 to 11, wherein the habitat is land planted with a crop.

13. A composition according to Claim 3 or 4, substantially as described in any of the foregoing Examples.

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14. A process for controlling undesirable plants which comprises applying to their habitat a composition as claimed in Claim 3, 4, 5, 6 or 12.

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